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PROCESS FOR MANUFACTURE OF FATTY ACID POLYOL ESTERS

[Verfahren zur Herstellung von Fettsäurepolyolestern]

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Description:

Area of the invention

[0001] The invention is in the area of the oleochemical raw materials and concerns an improved procedure for the production of polyol esters by transesterification of alkyl esters with polyols in the presence of a new catalyst system.

State of the art technology

[0002] Fatty acid polyol esters, whose alcohol components are derived for example from trimethylol propane or pentaerythritol, find various applications in the technology. They serve for example as cooling lubricants, in textile technology in the production of yarn and fibers, and also basis for production of cosmetic preparations. For their production, one proceeds usually from fatty acids or fatty acid alkyl ester, particularly the commercially available methyl ester to a large extent, which then in the presence of suitable catalysts, in which it often concerns heavy metal compounds, is subjected to a transesterification. In this connection, as an example, it is referred to the specifications WO 92/11271, WO 94/18163 as well as DE-C1 197 51 150. The achievement of high yields is thereby a rather secondary problem, which can be solved in case of doubt by influence of the law of mass action. Meanwhile it is quite difficult to manufacture esters, which meet the requirements of transesterification degree, acid carry-over number and in particular color quality. In this regard, catalysts stand out, like for example tin polish, zinc soaps or organozinc compounds; just these substances, which remain in the final product, both toxicologically and due to application technology reasons, are undesirable. The way out is to carry out the transesterification in the presence of usual bases, as for example, sodium hydroxide or sodium methylate; the resulting esters exhibit however, in particular, an inadequate color quality, which can hardly be improved separately by distillation, since in their course the color carriers remain in the sump, as the necessary high temperatures has to be developed again during the mass transfer.

[0003] The task of the present invention is to present an improved procedure for the production of fatty acid polyol esters, which

supplies products, which exhibit hydroxyl and acid factors of each below 5, preferably under 2 as well as Lovibond color factors (yellow, measured in the 51/4-bulb) of below 10, preferably under 5 and thus free from the initially described disadvantages.

Description of the invention

[0004] The subject of the invention is a procedure for the production of light colored fatty acid polyol esters by transesterification of fatty acid alkyl ester with polyols, which stand out by the fact that the reaction is carried out in the presence of reduction agents and alkali bases.

[0005] Surprisingly it was found that the use of combinations of reducing agents and alkali bases, particularly from complex hydrides and lithium bases, leads to the transesterification to fatty acid polyol esters, which fulfills the required profile.

Fatty acid alkyl ester

[0006] Fatty acid alkyl esters, which are considered in the context of the procedure according to invention as basic materials for transesterification, preferably follow the formula (I):

R^1COO-R^2 (I),

In the R^1CO for a linear or branched, saturated or unsaturated acyl radical with 6 to 22 carbon atoms and R^2 for a linear or branched alkyl residue with 1 to 4 carbon atoms. Typical examples are the ethyl-, propyl-, isomeric butyl- and in particular methyl ester of the caproic acid, caprylic acid, 2-ethyl hexonic acid, caprinic acid, lauric acid, isotridecanic acid, myristic acid, palmitic acid, palmoleinic acid, stearic acid, isostearic acid, oleic acid, elaidic acid, petroselinic acid, linolenic acid, linolenic acid, eleostearic acid, arachinic acid, gadoleic acid, behenic acid and erucic acid as well as their technical mixtures, which for e.g. are obtained in the compressive cleavage of natural fats and oils, in the reduction of aldehydes from the Roelen' oxo synthesis or the dimerization of unsaturated fatty acids. Besides so-called methyl esters of so-called "primary fatty acids" with 6 to 10 carbon atoms, esters of technical fatty acids with 12 to 18 carbon atoms, as for example, coke-, palm-, palm nut- or tallow fatty acid are preferred.

Polyols

[0007] In the sense of the procedure according to the invention, preferably such substances are considered as polyols, which are used for transesterification of the alkyl esters, which exhibit 2 to 12 carbon atoms and 2 to 6 hydroxyl groups. Typical examples are:

- Glycerine;
- Alkylene glycols, as for example, ethylene glycol, diethylene glycol, propylene glycol, butylene glycol, hexylene glycol, neopentyl glycol as well as polyethylene glycol with an average molecular weight of 100 to 1,000 Dalton;
- technical oligoglycerine mixtures with a self condensation degree of 1.5 to 10 as for instance technical diglycerine mixtures with a diglycerine content of 40 to 50 Wt. %;
- Methyol compounds, like in particular trimethylol ethane, trimethylol propane, trimethylol butane, pentaerythritol and dipentaerythritol;
- Low alkyl glucoside, in particular such with 1 to 8 carbons in the alkyl group, as for example methyl- and butyl glucoside;
- sugar alcohols with 5 to 12 carbon atoms, like for example sorbitol or mannitol;
- sugars with 5 to 12 carbons, as for example, glucose or saccharose;
- Amino sugar, as for example, glucamine;
- Dialcohol amines, like diethanolamine or 2-amino 1,3-dihydroxypropane.

[0008] Primarily glycerine, trimethylolpropane or pentaerythritol as well as their mixtures are used, whereby molecular ratio of alkyl esters to polyols - with reference to the hydroxyl groups available - can be 1:0.9 to 1:1.2.

Reducing agents

[0009] In the sense of the procedure according to the invention, hypophosphites or phosphites, as for example, sodium hypophosphite, primarily complex hydrides are considered as reducing agents. Typical examples of the last group are sodium boron hydride and/or lithium aluminum hydride. The application of sodium boron hydride is thereby particularly preferred, since it forms alkaline borate with the color carriers, in which it usually concerns carbonyl compounds, forms alkaline borate, which can work with alkali bases then as co-catalysts with sometimes synergistic increase in output. Usually the reducing agents are used in quantities of 0.001 to 2, preferably 0.002 to 0.5 Wt.% - with reference to application substances.

Alkali bases

[0010] Typically, alkali metal hydroxides and/or alcoholates are considered as alkali bases. Typical examples are sodium hydroxide, potassium hydroxide, sodium methylate, potassium methylate or potassium tert.-butylate, if necessary, in the form of alcoholic solutions. However, the use of lithium bases has proved to be advantageous, particularly lithium hydroxide and/or lithium methylate, since these exhibit a synergetic increase of the activity with the reducing agents, particularly the complex hydrides. Usually, the alkali bases are used in quantities of 0.001 to 2, preferably 0.002 to 0.5 Wt. % - with reference to the application substances.

Transesterification

[0011] The transesterification can be carried out in the known manner. Thereby the reactants if necessary, after drying process, are presented together with the catalyst system and heated up to a temperature in the range of 80 to 260, preferably 100 to 240°C. In order to shift the reaction to the side of the products, the released alcohol is continuously distilled, whereby the reduction of pressure to 100 to 900 mbar is recommended. After no more alcohol turns in, the pressure should be lowered to 10 to 100 mbar further, in order to remove unconverted initial ester from the product. After the transesterification, the polyol esters indicate an

acid number less than 2 and a hydroxyl number less than 5 as well as a Lovibond color value (yellow, measured in the 5 ¼"-cuvette) of less than 10, preferably less than 5.

Processing

[0012] If desired, still a processing and/or a refining of the polyol esters can follow the transesterification. This can take place for example in a bleaching with hydrogen peroxide solution, an alkaline treatment with caustic soda solution or a filtration in the presence of filtering agents. Primarily, the polyol esters are however distilled, which leads typically to an improvement of the color quality, since the raw material is already only slightly colored. Usually, the fatty acid polyol esters exhibit a Lovibond color number (yellow, measured in the 5¼"-cuvette) less than 5 after transesterification, bleaching and /or distillation.

Examples

Example 1

[0013] 1000 g (6 mol) of a technical mixture of methyl caprylate and methyl caprate were placed together with 223 g (1.66 mol) trimethylol propane in a 2-1-three-necked-flask and released at 80°C under decreased pressure of water traces. Subsequently, the mixture with 0.5 g of a 12 Wt. % sodium borohydride solution was added and agitated for 30 min. Thereafter, 0.5 g lithium hydroxide was added and the reaction mixture was initially heated at 235°C and then the pressure was reduced to 300 mbar, until the total quantity of liberated methanol was continuously removed. Finally, the pressure was lowered to 10 mbar to liberate the reaction product from unconverted methyl ester. Finally, the raw ester was bleached at 80°C by adding 0.3 Wt.-% 35 Wt.-% hydrogen peroxide, dried and filtered with addition of filtering agents. The resulting fatty acid trimethylol propane ester was bright, practically colorless and exhibited the following characteristic values: Sp = 0.4; OHZ = 0.9; Lovibond color in the 5¼"-cuvette (yellow) = 1.6.

Example 2

[0014] Similar to Example 1, 6 moles of the fatty acid methyl ester were converted with 153 g (1.66 moles) glycerin. The resulting fatty acid glycerin ester was bright, practically colorless and exhibited the following characteristic values: Sp =

0.1; OHZ = 1.9; Lovibond color in the 5¼"-cuevette (yellow) = 7.9. After one-step distillation at 260°C the Lovibond color number could be improved to 2.6.

Comparative example VI

[0015] Example 2 was repeated, however, the addition of the sodium boron hydride is dispensed with. The resulting fatty acid glycerin ester was bright, practically colorless and exhibited the following characteristic numbers: Sp = 0.1; OHZ = 6.9; Lovibond color in the 5¼-cuvette (yellow) = 38. After one-step distillation at 260°C the Lovibond color could be improved to 19.

Patent claims

1. Procedure for manufacture of light colored fatty acid polyol esters by transesterification of fatty acid alkyl ester with polyols is **characterized by** the fact that the reaction is carried out in the presence of reducing agents and alkali bases.
2. Procedure as per claim 1 is characterized by the fact that fatty acid alkyl esters of the formula (I) are applied:

R^1COO-R^2 (I),

In the R^1CO for a linear or branched, saturated or unsaturated acyl group with 6 to 22 carbon atoms and R^2 for a linear or branched alkyl group with 1 to 4 carbon atoms.
3. Procedure according to the claim 1 and/or 2 is characterized by the fact that fatty acid methyl esters are used.
4. Procedure according to at least one of the claims 1 to 3 is characterized by the fact that polyols are used, which are selected from the group, which is formed by glycerin, alkaline glycols, technical

oligoglycerine mixtures with a self-condensation degree from 1.5 to 10, methyol compounds, low alky glucosides, sugar alcohols, sugars with 5 to 12 carbon atoms, amino sugars and Dialcohol amines.

5. Procedure according to claim 4 is characterized by the fact that glycerin, trimethylol propane or pentaerythritol as well as their mixtures are used as polyols.

6. Procedure according to at least one of the claims 1 to 5 is characterized by the fact that complex hydrides, hypophosphites or phosphates are used as reducing agents.

7. Procedure according to claim 6 is characterized by the fact that sodium boron hydride and/or lithium aluminum hydride is used as reducing agent.

8. Procedure as per at least one of the claims 1 to 6 is characterized by the fact that the reducing agent is used in quantities of 0.001 to 2 Wt.-% - with reference to feedstock.

9. Procedure according to at least one of the claims 1 to 7 is characterized by the fact that alkali metal hydroxides and/or alcoholates are used as alkali bases.

10. Procedure according to claim 9 is characterized by the fact that lithium hydroxide and /or lithium methylate are used as alkali bases.

11. Procedure according to at least one of the claims 1 is characterized by the fact that the alkali bases are used in quantities of 0.001 to 2 Wt.-% - with reference to the feedstock.

12. Procedure according to at least one of the claims 1 to 11 is characterized by the fact that the transesterification is carried out at a temperature in the range of 80 to 260°C.

13. Procedure according to at least one of the claims 1 to 12 is characterized by the fact that the transesterification is carried out at a reduced pressure in the range of 1 mbar to 900 mbar.

14. Procedure according to at least one of the claims 1 to 13 is characterized by the fact that fatty acid polyol esters exhibit an acid number less than 2 and a hydroxyl number less than 5 after transesterification.

15. Procedure according to at least one of the claims 1 to 14 is characterized by the fact that the polyol esters exhibit a Lovibond coloring number (yellow, measured in the 5¼ -cuvette) of less than 10 after transesterification.

16. Procedure according to at least one of the claims 1 to 15 is characterized by the fact that the fatty acid

polyol esters are bleached and/or distilled after transesterification.

17. Procedure according to at least one of the claims 1 to 15 is characterized by the fact that the fatty acid polyol esters exhibit a Lovibond color factor (yellow, measured in the 5¼"-cuvette) of less than 5 after transesterification, bleaching and/or distillation.